Original Paper

Redox behaviour of polyvalent ions in phosphate glass melts and phosphate glasses[1)]

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Glass melts and glasses with the basic composition $NaPO_3 \cdot 2Sr(PO_3)_2$ doped with V_2O_5 and Fe_2O_3 were studied with the aid of square-wave voltammetry and spectroscopic methods. From the square-wave voltammetry in the glass melt, a linear dependence of the peak potentials on the temperature was obtained. The standard enthalpy ΔH^0, the standard entropy ΔS^0 and $lg(C_{ox}/C_{red})$ of the transitions Fe^{3+}/Fe^{2+} and V^{4+}/V^{3+} were calculated. The diffusion coefficients calculated from the peak currents measured follow Arrhenius' law. By means of electron spin resonance, the concentration of V^{4+} was determined. The corresponding extinction coefficients for the V^{4+} bands were calculated from the absorption spectra. Concerning the vanadium-containing glass, the results of square-wave voltammetry and spectroscopy were compared quantitatively. For the iron-doped glass, the comparison was only qualitative.

Redoxverhalten polyvalenter Ionen in Phosphatglasschmelzen und Phosphatgläsern

Es wurden Gläser der Zusammensetzung $NaPO_3 \cdot 2Sr(PO_3)_2$ mit Eisen und Vanadium dotiert und mit Hilfe der Square-Wave-Voltammetrie und der Spektroskopie untersucht. Aus den Messungen der Square-Wave-Voltammetrie konnte ein linearer Zusammenhang des Peakpotentials in Abhängigkeit von der Temperatur erhalten werden. Die Standardenthalpie ΔH^0, die Standardentropie ΔS^0 und $lg(C_{ox}/C_{red})$ der Übergänge Fe^{3+}/Fe^{2+} und V^{4+}/V^{3+} wurden daraus berechnet. Aus den Peakströmen wurden die Diffusionskoeffizienten erhalten, die Arrheniussches Verhalten zeigen. Die Konzentration an V^{4+} wurde mittels Elektronenspin-resonanz-Spektroskopie bestimmt und die Extinktionskoeffizienten der V^{4+}-Bande wurden aus dem Absorptionsspektrum berechnet. Die Ergebnisse aus der Square-Wave-Voltammetrie und der Spektroskopie wurden verglichen, für das vanadiumhaltige Glas quantitativ und für das mit Eisen dotierte Glas qualitativ.

1. Introduction

Many properties of the glass melt and the glass product are influenced by the type and the concentration of polyvalent ions [1 to 3]. Examples of such properties of the glass melt are the solubility of gases and the refining behaviour; for the final glass product the transmission or colour are decisive. The investigation of the redox behaviour can be carried out directly in the glass melt with the aid of square-wave voltammetry (SWV) [4 and 5]. By means of optical and electron spin resonance (ESR) spectroscopy, the redox ratio of the polyvalent ions can be determined in the quenched glass.

In the glass melt, the polyvalent elements and the physically dissolved oxygen are in equilibrium. The redox reaction of the polyvalent elements can be described as follows:

$$M^{(x+n)+} + \frac{n}{2} O^{2-} \rightleftharpoons \frac{n}{4} O_2 + M^{x+} \qquad (1)$$
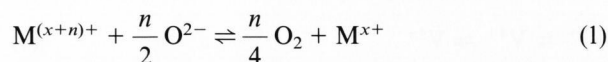
The equilibrium constant $K(T)$ is defined as

$$K(T) = \frac{[M^{x+}]}{[M^{(x+n)+}]} [O_2]^{n/4} \qquad (2)$$

and depends on both the glass composition and the temperature. The standard free enthalpy ΔG^0 of the redox reaction can be calculated from the equilibrium constant:

$$\Delta G^0(T) = -RT \cdot \ln K(T) = \Delta H^0 - T \cdot \Delta S^0 = -nF \cdot E^0(T). \qquad (3)$$

From the temperature dependence of $E^0(T)$, measured by means of SWV, the standard enthalpy ΔH^0 and the standard entropy ΔS^0 can be calculated. Square-wave voltammograms are current–potential curves which exhibit distinct peaks caused by the polyvalent element present. The peak current is a function of temperature and of the experimental parameters: the pulse time τ and the pulse amplitude ΔE:
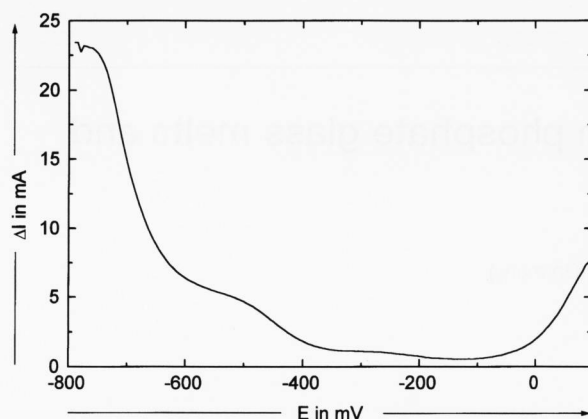
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Figure 1. Experimental square-wave voltammogram of an undoped phosphate glass melt (τ = 5 ms, ΔE = 100 mV, ϑ = 1000 °C).

$$\Delta I_p = 0.31 \frac{A \, C_0 \, n^2 \, F^2 \cdot \Delta E}{R\,T} \sqrt{\frac{D}{\tau \pi}} \qquad (4)$$

From the peak current, ΔI_p, the self-diffusion coefficient, D, of the polyvalent ions can be determined if the total bulk concentration of the polyvalent element, C_0, the number of electrons transferred, n, and the surface area A of the electrode are known. The diffusion coefficients depend on temperature following Arrhenius' law:

$$D = D_0 \, e^{-E_D/(R\,T)} . \qquad (5)$$

where E_D is the activation energy of the self-diffusion process. For a more detailed description of the theory of SWV see [6 and 7].

The combination of two spectroscopic methods enables the determination of the redox state. The V^{4+} concentration can quantitatively be determined using ESR. If the V^{4+} concentration is known, the extinction coefficient of the V^{4+} bands in the absorption spectra can be calculated according to the law of Lambert-Beer:

$$E(\lambda) = \varepsilon(\lambda) \cdot c \cdot d . \qquad (6)$$

In addition, this paper provides a comparison of the results from SWV and spectroscopic measurements.

2. Experimental

The glasses with the basic composition $NaPO_3 \cdot 2Sr(PO_3)_2$ were modified by adding 0.5 wt% iron as Fe_2O_3 and 0.5 wt% vanadium as V_2O_5. The SWV measurements were carried out in the temperature range of 750 to 1000 °C in a resistance-heated furnace with a vertical alumina tube. In the middle of this furnace, the platinum crucible with the glass melt was located, in which three electrodes were inserted: a platinum wire acting as working electrode, a platinum plate as counter electrode and the reference electrode which was a ZrO_2

probe flushed with air. All potentials mentioned in this paper are referred to the ZrO_2/air electrode. The experimental equipment and procedure are described in detail in [8].

For spectroscopic investigations, the base glass was melted in a silica crucible at 1200 °C. Powdered glass samples were remelted at different temperatures in the range of 900 to 1300 °C for 1 h. The glass, doped with V_2O_5 was melted under either reducing or oxidizing conditions. To reduce the vanadium in the glass, the melt was doped with 1 wt% sugar. Oxidizing conditions were established by bubbling O_2 for 1 h through the melt at 1200 °C. All melts were quenched and cooled down to room temperature. For absorption measurements, the glasses were ground to plates of 1 mm thickness and polished. The optical absorption spectra were recorded in the range of 190 to 3200 nm using a double-beam spectrometer (UV-3101 PC, Shimadzu Corp.). The ESR spectra of powder samples were obtained by a spectrometer ZWG ERS 210 (error <10%).

3. Results and discussion

In figure 1, a voltammogram of a dopant-free phosphate glass (P) is shown. An increase in the current can be observed at potentials higher than 0 mV due to the formation of O_2 at the working electrode. At potentials lower than −700 mV, the increase in current is caused by the decomposition of the posphate glass matrix. In addition, a slight peak at −580 mV is visible [9]. This peak was also observed in phosphate glasses of other compositions as well as in fluoride phosphate glasses (FP) with 10 mol% phosphate. Since phosphate glasses posses a higher water content (in form of OH^- groups) than the most silicate glasses [10], this peak may be caused by the reduction of the highly mobile OH^- ions [11] to gaseous hydrogen. On the other hand, this peak occurs in FP glasses whose water content is low and comparable with silicate glasses. SWV investigations of bubbled P glass melts did not show any decrease in the peak currents of the voltammograms whereas, concerning the IR spectra, a distinct decrease in the intensity of the OH bands was obtained. Based on these contrary findings, another explanation is possible: the phosphate is reduced to elemental phosphorus and at higher potentials to the thermodynamically favoured PH_3 according to the following redox reaction scheme:

$$P^{5+} \leftrightharpoons P^0 \leftrightharpoons P^{3-} . \qquad (7)$$
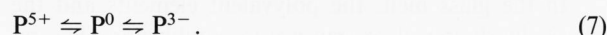
In figure 2a, the voltammogram of the vanadium-containing glass at 1000 °C is presented. A well-pronounced peak at −350 mV can be observed. For vanadium, two redox reactions are possible:

$$V^{5+} \leftrightharpoons V^{4+} \leftrightharpoons V^{3+} . \qquad (8)$$
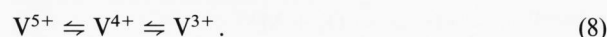
From ESR it is known, that vanadium in P glasses mainly occurs in the redox state V^{4+}. Therefore, the peak observed in figure 2a is attributed to the reduction

of V^{4+} to V^{3+}. The V^{5+}/V^{4+} transition is indicated at positive potentials, but is superimposed by the increase in current caused by the formation of oxygen.

In figure 2b, the voltammogram of iron in the P glass melt recorded at 1000°C is shown. The peak at a potential of -170 mV is caused by the reduction of Fe^{3+} to Fe^{2+}. The shoulder at around -600 mV corresponds to the small peak observed in figure 1 [9]. The reduction of Fe^{2+} to metallic iron is not detectable because the attributed potential is more negative than that of the phosphate glass matrix.

Figure 3 demonstrates the linear dependence of the peak potentials upon the temperature. With increasing temperature, the V^{3+} content increases slightly, caused by the small changes of $E_p(T)$. To form higher amounts of V^{3+} in the glass, strongly reducing conditions are required. Because of the steeper slope of the $E_p(T)$ curve, changes of the temperature have more influence on the redox ratio of iron than on that of vanadium. According to equation (3), the standard enthalpies, the standard entropies and $\lg(C_{ox}/C_{red})$ for equilibrium with air were calculated. The diffusion coefficients were obtained from the corresponding peak currents using equation (4). As seen in figure 4, D depends linearly on the reciprocal temperature. From the Arrhenius' equation (6) the activation energy, E_D, was calculated from the slope of the linear regression line [12]. In table 1, all values obtained from SWV are summarized.

By means of ESR spectroscopy, paramagnetic substances can be investigated [13]. In figure 5 the ESR spectrum of the vanadium-containing glass is presented. The only redox state of vanadium providing an ESR signal is the V^{4+} ion due to its single unpaired spin with the electron configuration $3d^1$ [14]. All glasses doped with vanadium and melted under different conditions were investigated by ESR to determine the V^{4+} content. The concentration of V^{4+} can be calculated by the integration of the observed signal and by comparison with a standard substance with known number of spins. From the isotropic hyperfine splitting of the ESR spectrum, interpretations of the bonding in the vanadyl complexes are possible [14 to 16].

Figure 6 illustrates the temperature dependence of the redox behaviour by means of results from both SWV and ESR. For the calculation of the $\lg(C_{ox}/C_{red})$ values from ESR measurements, the assumption was made that vanadium solely occurs in the redox states V^{3+} and V^{4+}. With respect to SWV, it was assumed that at the corresponding temperature equilibrium was obtained. The results from SWV in the melt were in good agreement with the values obtained in the cooled glass by ESR. Hence, it can be concluded that the redox ratio remains constant during cooling to room temperature.

In figure 7a, the absorption spectrum of the vanadium-containing glass is shown with the different absorption bands of V^{4+}: a $^2T_1 \rightarrow {}^2E$ transition at 680 nm and a $^2T_1 \rightarrow {}^2T_2$ transition at 870 nm. In the glass, the V^{4+} ion may exist in sixfold coordination with a tetra-
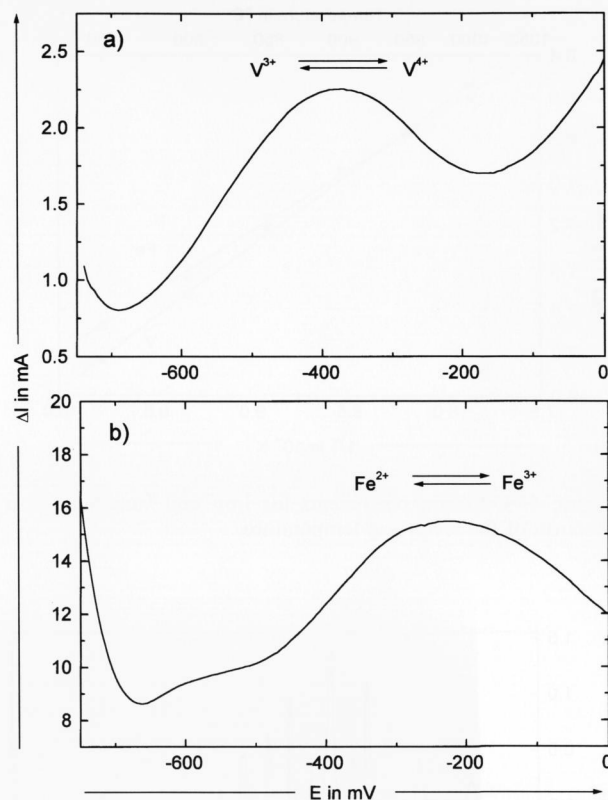
Figures 2a and b. Experimental square-wave voltammogram in phosphate glass melts; a) doped with V_2O_5 ($\tau = 100$ ms, $\Delta E = 100$ mV, $\vartheta = 1000$°C), b) doped with Fe_2O_3 ($\tau = 10$ ms, $\Delta E = 100$ mV, $\vartheta = 1000$°C).
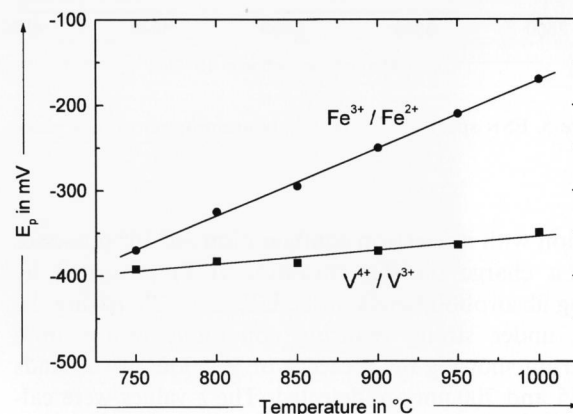

Figure 3. Peak potentials as a function of temperature for the transitions V^{4+} to V^{3+} and Fe^{3+} to Fe^{2+}.

gonal distortion from octahedral symmetry as vanadyl complex (VO^{2+}) [17]. The bands of the d – d transitions were fitted as Gauß curves and the corresponding extinction coefficients were calculated according to equation (7) using the V^{4+}-concentration determined by ESR.

Figure 7b illustrates the changes in the absorption spectra caused by different melting conditions. Bubbling with O_2 leads to a decrease in the intensity of the V^{4+} bands indicating the formation of V^{5+} in the glass. The
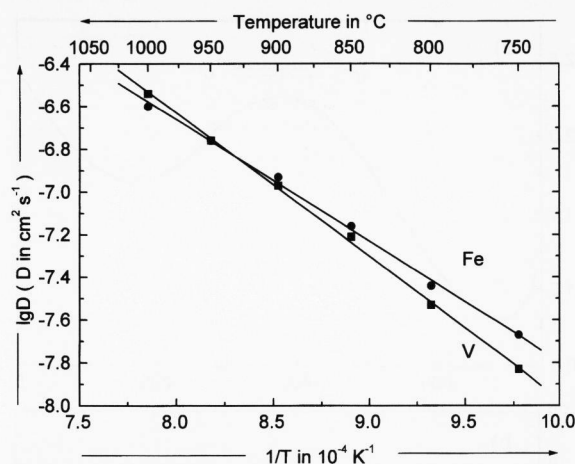
Figure 4. Diffusion coefficients for iron and vanadium as a function of the reciprocal temperature.
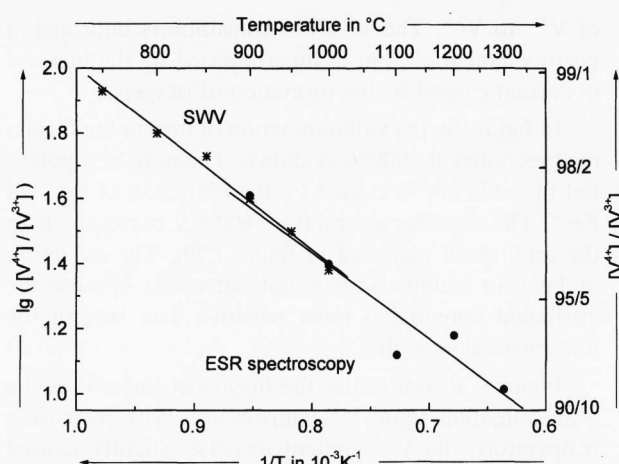

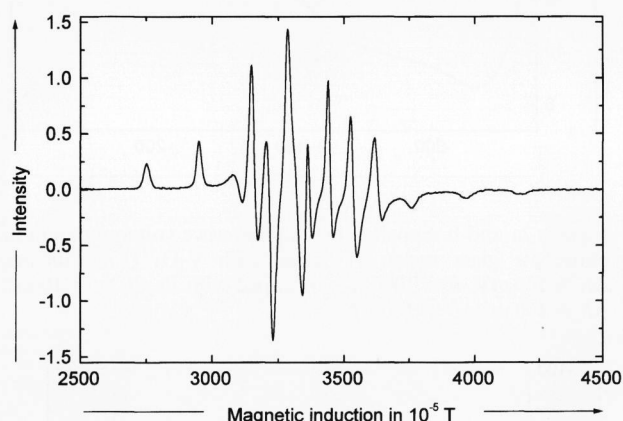Figure 6. Comparison of the results from ESR and SWV for the vanadium-containing glass.

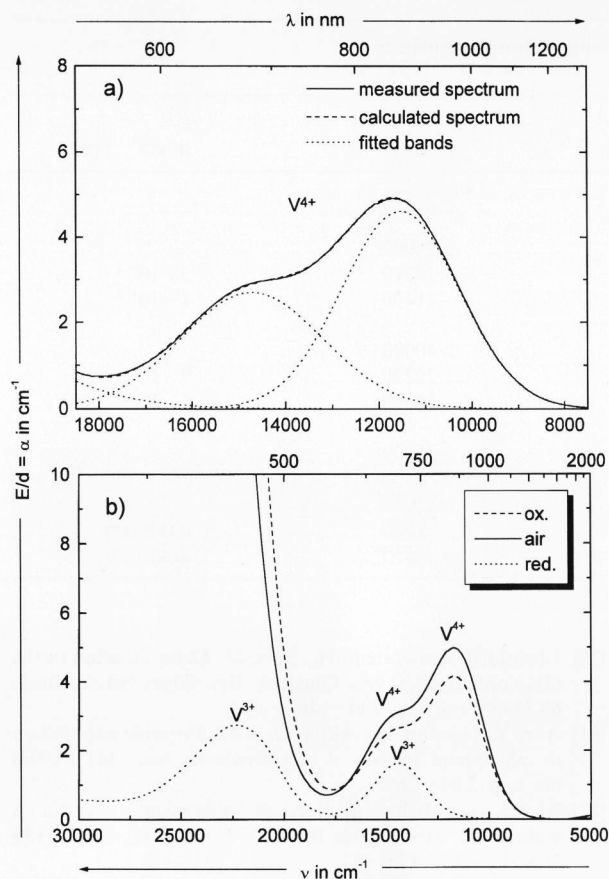Figure 5. ESR spectrum of the V^{4+} containing phosphate glass.

V^{5+} ion with its electron configuration $3d^0 4d^0$ possesses only a charge transfer transition (CT) presented by strong absorption bands in the UV range. Preparing the glass under strong reducing conditions results in a spectrum showing the presence of V^{3+} ions. Two bands at 445 and 700 nm are detected. The ε values were calculated for the $^3T_{1g} \rightarrow {}^3T_{2g}$ and the $^3T_{1g} \rightarrow {}^3T_{2g}(P)$ transitions. The band of the charge transfer transition of V^{3+} was observed only as UV edge since the concentration of V^{3+} in the glass was too high to obtain a well-distinguishable peak. The determination of ε of this band is only possible in glasses with low concentration of

dopants [18 and 19]. In table 2, the redox states of vanadium in the glass melted under different conditions and investigated by different methods are shown.

In figure 8a, the absorption spectrum of the iron-containing glass is presented. The Fe^{2+} ion causes two absorption bands in the NIR region, and CT transition. By contrast, the Fe^{3+} ion causes only a transition in the UV region detected as absorption edge. The Fe^{2+} bands of the d−d transitions were fitted: the peak at 1020 nm is attributed to the Fe^{2+} ion in octahedral coordination and the band near 2200 nm is caused by Fe^{2+} in tetrahedral coordination [19 and 20]. The band at 2200 nm is strongly influenced by the OH bands. The ε values of the bands were not calculated since the determination of the Fe^{2+} concentration was impossible because it was present in different coordinations. Therefore, the temperature dependence of the spectra can only be discussed qualitatively (see figure 8b). With decreasing temperature, the intensity of the Fe^{2+} decreases. With rising temperature (above 1100 °C), the difference in the band intensities becomes more distinct. A possible explanation for this behaviour could be that the melting time was too short to reach equilibrium, or else a change in the coordination of Fe^{2+} occurred. The latter could not be proved since the OH band influences the band of the tetrahedrally coordinated Fe^{2+}. For the samples melted at 1000 and 900 °C, the OH content is high enough to notably influence the Fe^{2+} band at 2200 nm. In table 3, all values obtained from absorption spectroscopy are summarized.

Table 1. Calculated values from SWV ($\vartheta = 1000\,°C$, $p_{O_2} = 0.21$ bar)

transition	E_p in mV	ΔH^0 in kJ/mol	ΔS^0 in kJ/mol	$\lg(C_{ox}/C_{red})$	$\lg D$ (D in cm²/s)	E_D in kJ/mol
V^{4+}/V^{3+}	−350	58	15	1.38	−6.5	129
Fe^{3+}/Fe^{2+}	−170	125	82	0.67	−6.6	107

Figures 7a and b. Absorption spectra of the phosphate glass doped with V_2O_5; a) V^{4+} spectrum and fitted bands, b) absorption spectra of the V^{4+}-containing phosphate glass melted under different conditions.
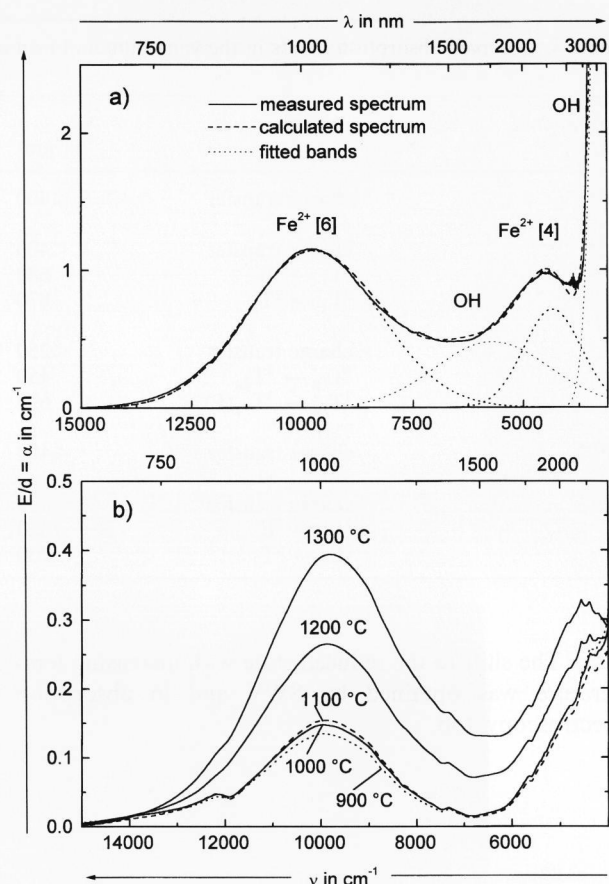
Figures 8a and b. Absorption spectra of the phosphate glass doped with Fe_2O_3; a) Fe^{2+} spectrum and fitted bands, b) absorption bands for the Fe^{2+} in octahedral coordination measured as a function of the melting temperature.

Table 2. Redox ratios of vanadium melted under different conditions

melting condition	melting temperature in °C	vanadium concentration (in %) determined with						
		SWV			ESR	AS		
		V^{5+}	V^{4+}	V^{3+}	V^{4+}	V^{5+}	V^{4+}	V^{3+}
oxidizing	1200				70	31	69	–
air	1200				94	–	94.5	5.5
air	1100				93	–	95	5
air	1000	–	96	4	96	–	95	5
air	900	–	98	2	98	–	97	3
reducing	1200				1	–	1	99

4. Conclusions

SWV measurements revealed that the redox ratio is shifted to the reduced state with increasing temperature. For vanadium, the temperature dependence of E_p is slightly indicating that the V^{4+} ion is a very stable redox state in the phosphate glass melt. This was also observed using spectroscopy. Melting at different temperatures leads only to small changes in the V^{4+} content determined by ESR and from the absorption spectra. The results from SWV in the melt are in good agreement with the results from ESR. Caused by the stable V^{4+} ion, the formation of V^{3+} requires strongly reducing conditions. To obtain V^{5+} in the glass, oxidizing conditions, e.g. bubbling of O_2 through the melt, are necessary. The iron redox ratio is influenced by the temperature to a higher extent than the vanadium redox

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Table 3. Observed absorption bands in the vanadium and iron containing phosphate glasses

polyvalent ion	transition	λ in nm	ν in cm^{-1}	ε in cm^{-1} ppm^{-1}
V^{5+}	charge transfer	<400	>25000	
V^{4+}	charge transfer	<400	>25000	
	$^2T_1 \rightarrow {}^2E$	680	14710	$3 \cdot 10^{-4}$
	$^2T_1 \rightarrow {}^2T_2$	870	11490	$1 \cdot 10^{-3}$
V^{3+}	charge transfer	<250	>40000	
	$^3T_{1g} \rightarrow {}^3T_{2g}$	450	22220	$9 \cdot 10^{-4}$
	$^3T_{1g} \rightarrow {}^3T_{1g}(P)$	690	14490	$5 \cdot 10^{-4}$
Fe^{3+}	charge transfer	<400	>25000	
Fe^{2+}	charge transfer	<400	>25000	
	$^5T_2 \rightarrow {}^5E$	1020	9800	unknown
	$^5E_2 \rightarrow {}^5T_2$	≈ 2200	≈ 4550	unknown

ratio. The shift to the reduced state with increasing temperature was obtained by SWV and in absorption spectroscopy, too.

5. References

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